

Synthesis, Characterization of $\text{Cu}_{0.5}\text{Co}_{0.5}\text{WO}_4$ and its application on Cr(VI) removal in aqueous medium

S. Prabhu^a, R. Udhayakumar^a, K. Jeganathan^b and K. Jothivenkatachalam^a

^aDepartment of Chemistry,
Anna University, BIT-Campus, Tiruchirappalli, Tamilnadu, INDIA.

^bCentre for Nanoscience and Nanotechnology,
School of Physics, Bharathidasan University, Tiruchirappalli, Tamil Nadu, INDIA.
email:jothivenkat@yahoo.com

*Presented in First National Conference on Thin Film Science and Nano Technology
(FIRST-NCTFSANT-2013) September 2-3, 2013, Rajah Serfoji Govt. College, Thanjavur, T.N.(India).*

ABSTRACT

We report the synthesis of multi-metal component $\text{Cu}_{0.5}\text{Co}_{0.5}\text{WO}_4$. The synthesized sample was characterized by FT-IR, UV-DRS, XRD, EDX and FESEM analysis. The average particle and crystalline size was calculated using FESEM and XRD techniques respectively. The surface area of the sample was measured using BET techniques. Furthermore, The sample was used to efficient removal of Cr(VI) in aqueous medium.

Keywords: Multi-metal component, $\text{Cu}_{0.5}\text{Co}_{0.5}\text{WO}_4$, adsorption, Cr(VI) removal.

1. INTRODUCTION

A “Multi metal component” oxide like divalent metal tungstates ($\text{M}^{\text{II}}\text{WO}_4$) has gained additional importance due to its wide application in various fields. Nanostructured tungstate based materials are known for their wide applications in conventional catalysis, or as scintillator material and in photoluminescence.^{1, 2} Cr(VI), existing in most aquatic environments, which is highly

toxic and environmentally harmful. Therefore, the development of technologies to prevent further chromium discharge and remediate Cr(VI) contamination are of great importance. The conventional methods to remove Cr(VI) from wastewater are chemical redox, followed by precipitation, concentration, evaporation, reverse osmosis, biosorption, ion exchange, adsorption, solvent extraction and membrane separation³⁻⁷. A major drawback of precipitation is sludge

production. Ion exchange and reverse osmosis are high operating costs⁸. Among the above methods, adsorption is highly efficient and economical, and therefore, it is a promising technique for the removal of Cr(VI) from wastewater.

Herein, we report the synthesis of $\text{Cu}_{0.5}\text{Co}_{0.5}\text{WO}_4$ catalyst. The synthesized sample was characterized by FT-IR, UV-DRS, XRD, EDX and FESEM analysis. The average particle and crystalline size was calculated using FESEM and XRD techniques respectively. The surface area of the sample was measured using BET techniques. The prepared catalyst was utilized as an adsorbent to efficient removal of Cr(VI) in aqueous medium.

2. EXPERIMENTAL

2.1 Preparation of catalyst

The $\text{Cu}_{0.5}\text{Co}_{0.5}\text{WO}_4$ component was prepared by co-precipitation method as reported in literature⁹. Stiocheiometric amount of metal salts were made separately in distilled water to obtain a clear solution. Aqueous solutions were mixed and precipitated as metal tungstates and cooled for 1–2 h. The obtained precipitate was calcinated at 500 °C for 5 h in muffle furnace.

2.2 Characterization of catalyst

FT-IR analyses were performed using Jasco FT-IR 460 plus model spectrophotometer. UV-vis Diffuse reflectance spectra (DRS) were recorded on Shimadzu UV 2450 UV-Visible Spectrophotometer. X-ray Diffraction (XRD) measurement was carried out with

Bruker AXS Model D8 Advance System using Cu K α radiation. The Field Emission scanning electron microscope (FESEM) image was obtained using Carl Zeiss SIGMA. The Energy dispersive X-ray spectra (EDX) recorded on INCAX-act Oxford Instruments. The BET surface area was measured using ASAP 2020 Micromeritics instrument.

2.3 Removal of Cr(VI)

The stock solution was made by dissolving 50 mg/L of $\text{K}_2\text{Cr}_2\text{O}_7$ in distilled water. For the removal experiment, 25 mg of the catalyst was suspended in 50 ml of the stock solution and stirred in dark at pH 3. At the given time interval 3 ml of the sample solution was taken and centrifuged to remove the catalyst. The solution was analyzed by recording UV-Vis spectra on the spectrophotometer and the concentration of Cr(VI) was determined at its characteristic absorption wavelength of 350 nm.

3. RESULTS AND DISCUSSION

3.1. Characterization of the catalyst

3.1.1. Crystalline nature

The XRD pattern of the prepared sample was well matched with the reported data by ICDD data card (JCPDS No.: 72-0479) and literature report⁹ (Fig. 1(a)). Metal tungstate, Co/CuWO_4 is the wolframite type structure, in which oxygen atoms are in hexagonal closed pack arrangement and $\text{Co}^{2+}/\text{Cu}^{2+}$ and W^{6+} cations are filled in octahedral sites^{10,11}. The average size of the

crystal was estimated by Scherrer formula¹² (given in eqn 1) of the sample is 30 nm.

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where D is the crystalline size, K is constant equal to 0.9, λ is wavelength of the radiation used (1.5406 Å), β is the FWHM (full width half maximum) in radians on the 2θ and θ is Bragg angle for the diffraction peak. Based on the eqn (1), the calculated crystalline size

3.1.2. FT-IR study

The FT-IR spectra of the sample are shown in Fig. 1(b). The absorption band around 890 cm^{-1} can be assigned to WO_4 tetrahedron W-O stretching mode^{13,14}. The Co/Cu-O stretching band can be observed around 800 cm^{-1} . The absorption band below 600 cm^{-1} can be attributed to the deformation of W-O or W-O-W bridges¹⁵.

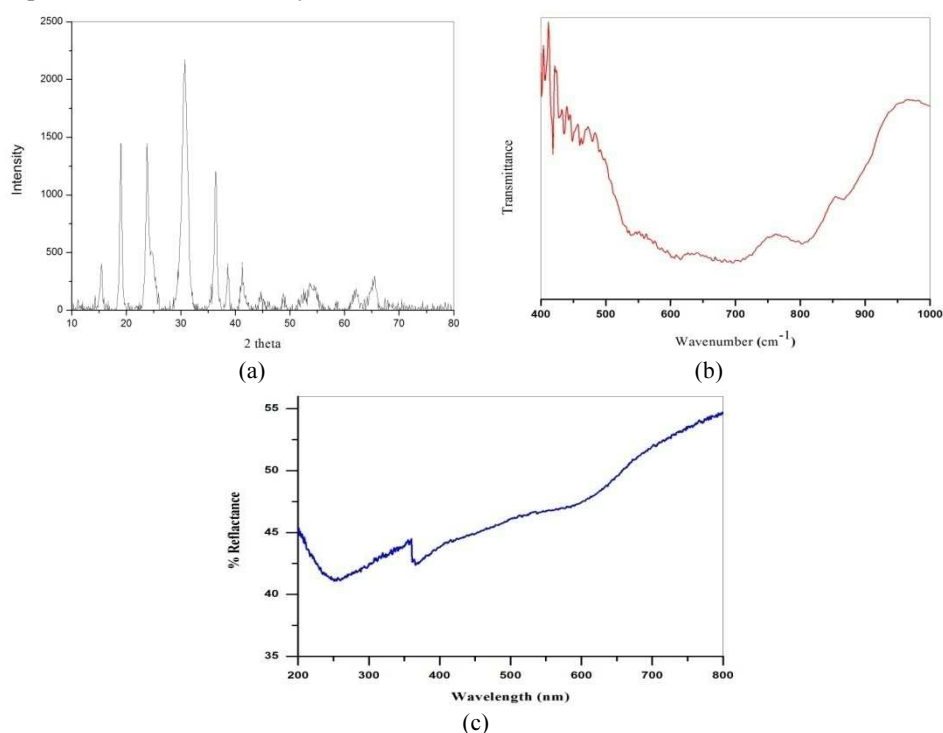


Fig. 1. (a). XRD, (b). FT-IR, (c). UV-Vis spectrum of the catalyst

3.1.3. Optical property

The optical property of the sample was studied by the UV-vis spectroscopic technique. The UV-Vis diffused reflectance spectra of the prepared samples are shown in Fig. 1(c). The spectra shows very broad line

which can be attributed to the presence of consecutive energy levels in the sample.

3.1.4. Morphological study

The surface morphology of the sample was studied by FESEM analysis and

shown in Fig. 2(a). The very fine spherical particles with the average size of 33 nm were observed in the FESEM images. The elemental composition present in the sample was investigated by recording EDX

spectrum and shown in Fig. 2(b). The EDX analysis confirmed the elements Cu, Co, W and O present in the sample. The measured BET surface area of the sample is 27.0516 m²/g.

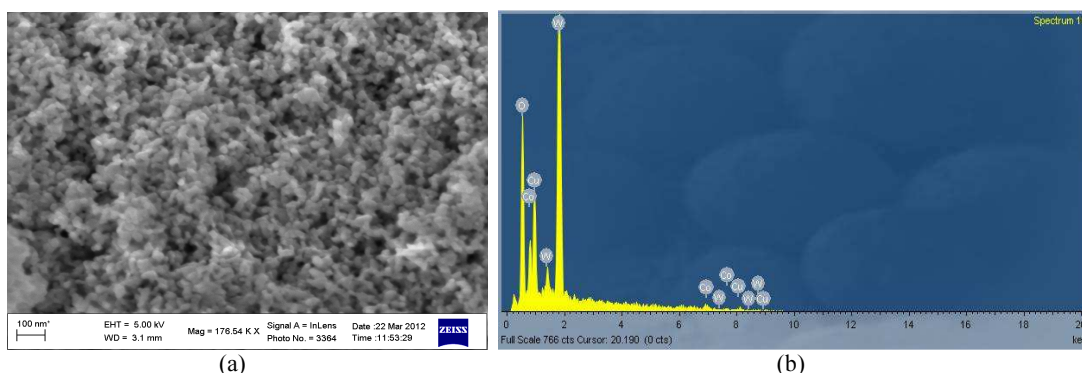


Fig. 2. (a). FESEM image and (b) EDX spectrum of the catalyst

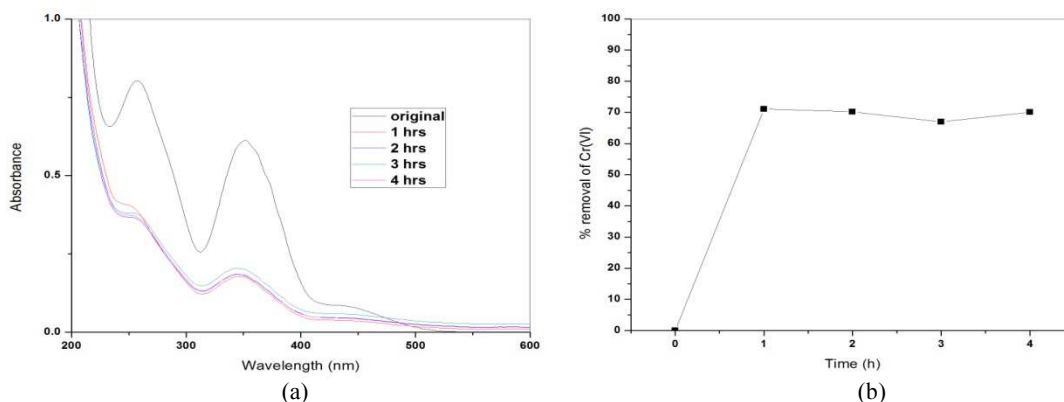


Fig. 3. (a). Temporal UV-Vis changes of Cr(VI) solution, (b). % removal of Cr(VI) by the catalyst

3.2. Removal of Cr(VI)

The temporal UV-Vis absorption spectrum for the removal of Cr(VI) was shown in Fig. 3(a) which shows that, the maximum adsorption on the catalyst surface was achieved within 1 hr. The % removal efficiency of the catalyst was calculated using the following formula,

$$\% \text{ removal} = (A_0 - A_t) / A_0 \times 100$$

Where, A_0 and A_t are the absorbance intensities at initial and at time t , respectively.

The % removal efficiency of the catalyst was shown in Fig. 3(b). The maximum adsorption of around 70 % was observed. The adsorption process almost

finished within 1 hr, and no significant change was observed from 1 hr to 4 hr which shows the strong adsorption capacity of the catalyst rather than the desorption occurred.

4. CONCLUSION

The catalyst $\text{Cu}_{0.5}\text{Co}_{0.5}\text{WO}_4$ synthesized and well characterized by FT-IR, UV-DRS, XRD, EDX and FESEM techniques. The catalyst was used as an adsorbent to remove the Cr(VI) in aqueous medium. The high removal percentage of about 70 % was attained within 1hr. There is no significant desorption was observed after 1 hr. This results suggest that, the catalyst can be efficiently utilized as a adsorbent for the removal of Cr(VI). Supplementary experimental analysis is needed to further understanding on the efficiency and nature of the catalyst which is under progress.

REFERENCES

1. Pullar, R. C.; Farrah, S. Alford, N. M. *J. Eur. Ceram. Soc.*, 27, 1059 (2007).
2. J. Lin, J. Lin, Y.F. Zhu, *Inorg. Chem.*, 46, 8372 (2007).
3. Y. Xing, X. Chen, D. Wang, *Environ.Sci. Technol.* 2007, 41, 1439.
4. V. Sarin, K.K. Pant, *Technol.* 97, 15 (2006).
5. Y.C. Sharma, C.H. Weng, *J. Hazard. Mater.*, 142, 449 (2007).
6. A. Ramesh, H. Hasegawa, T. Maki, K. Ueda, *Sep. Purif. Technol.*, 56, 90 (2007).
7. Z. Reddad, C. Gerente, Y. Andres, P. Cloirec, *Environ. Sci. Technol.*, 36, 2067 (2002).
8. J. Hu, I. M. C. Lo, G. Chen, *Langmuir*, 21, 11173 (2005).
9. S.J. Naik, A.V. Salker, *Catalysis Communications*, 10, 884 (2009).
10. T. Mathew, N.M. Batra, S.K. Arora, *J. Mater. Sci.*, 27, 4003 (1992).
11. L.J. Bucham, I.E. Wachs, *Spectrochim. Acta A*, 54, 1355 (1998).
12. M. Galceran, M.C. Pujol, C. Zaldo, F. Daz, M. Aguil, *J. Phys. Chem. C*, 113, 15497 (2009).
13. Y. Gao, J. Zhao, Y. Zhu, S. Ma, X. Su, Z. Wang, *Mater. Lett.*, 60, 3903 (2006).
14. H. Zhang, Xijun Hu, *Separ. Purif. Technol.*, 34, 105 (2004).
15. Tomaszewicz, *Thermo Chim. Acta*, 447, 69 (2006).